

Cell Analysis, Modeling, and Prototyping (CAMP) Facility Research Activities

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Project ID:
ES030

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Overview

Timeline

- Start: October 1, 2012
- Finish: September 30, 2014
- ~75% Complete

Budget

- \$2,000 K for FY14
 - 100% DOE-ABR
- \$2,500 K for FY13
- Restructured as a DOE core-funded effort in FY13

Barriers

- Need a high energy density battery for PEV use that is safe, cost-effective, and has long cycle life.
 - Independent validation analysis of newly developed battery materials are needed in cell formats with at least 0.2 Ah before larger scale industrial commitment

Partners

- Sandia and Oak Ridge National Labs
- Illinois Institute of Technology
- University of Illinois
- Purdue University
- University of Rochester
- See industrial list at end

Relevance/Objectives

- Transition new high energy battery chemistries invented in research laboratories to industrial production through independent validation and analysis in prototype cell formats (xx3450 pouch & 18650 cells).



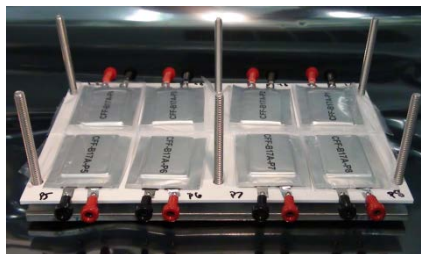
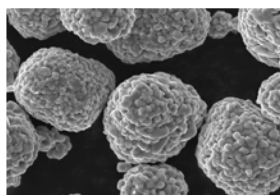
- Researchers are often not able to provide the quantities of novel materials needed to make a full size PEV cell to demonstrate the merits of their discoveries. The CAMP Facility is ideally sized to explore new materials with quantities as small as 50 grams for active materials, and even less for electrode/electrolyte additives.
- Today's talk will focus on silicon-based anodes and LMR-NMC cathodes.

FY14 Milestones

Date	Milestone Description	Status
12/31/2013	Initiate integration of interfacial impedance and bulk transport models into full cell	Completed
12/31/2013	Assess performance of PVDF separator vs. polyolefin	Completed
3/31/2014	Determine n:p ratio effect on performance for LMR-NMC vs. Graphite	Completed
3/31/2014	Determine effect of current rate on cycle life for LMR-NMC vs. graphite	Completed
6/30/2014	Recommend formation process for LMR-NMC based cells that use bifunctional electrolyte additives	On Schedule
6/30/2014	Recommend optimal electrode thickness based on electrochemical model and verified via experiment	On Schedule
9/30/2014	Submit report on recommended electrolyte additives and electrode composition for high energy lithium ion electrochemical couples (e.g. LMR-NMC cathode and silicon based anodes)	On Schedule
9/30/2014	Submit final report on advanced battery materials validated in FY14 and summary of Electrode Library activity	On Schedule
9/30/2014	Advance development of electrochemical models and enhance battery design and cost models focusing on high energy lithium ion electrochemical couples (e.g. LMR-NMC positive and silicon/graphite negative electrodes)	On Schedule
9/30/2014	Fabricate pouch cells using silicon based anode and high energy cathode (e.g. LMR-NMC)	On Schedule

Approach

- Researchers submit materials with promising energy density
 - Small hand-coated electrodes are made
 - Coin cells are made and tested
- } Glove box
Benchtop
- Larger material samples are obtained (MERF, partnerships, etc.)
 - Longer lengths of electrode are made from scaled materials
 - Pouch cell or 18650s are made and tested
- } Dry Room
Pilot scale
- Extensive diagnostics and electrochemical modeling on promising technologies



Technical Accomplishments

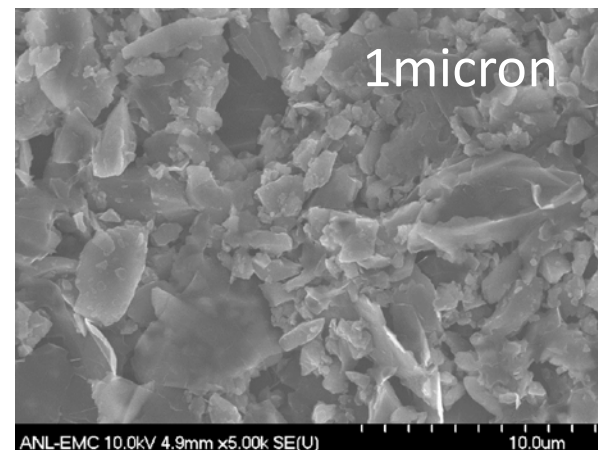
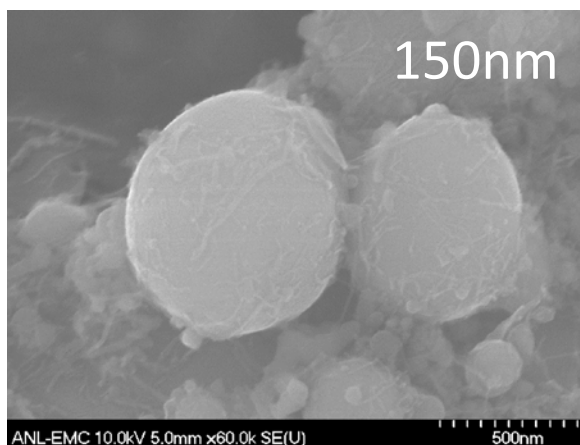
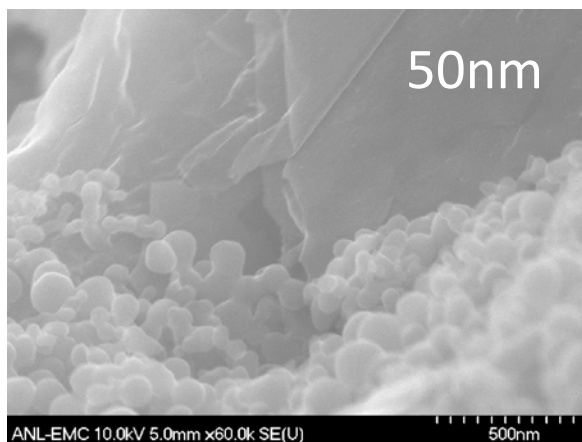
- Secured several sources of battery grade silicon powders
- Fabricated preliminary pouch cell build with silicon-based anodes
- Secured Superior Graphites' SLC1520P as new CAMP graphite anode baseline
- Confirmed benefit of electrolyte additives in pouch cells for LMR-NMC
- Fabricated interim pouch cell build for DOE-EERE Award – Miltec UV
- Fabricated baseline electrodes and pouch cell for DOE-EERE Award – Argonne
- Supplied numerous electrodes via Electrode Library and expanded its offerings
- Determined effect of Negative to Positive capacity ratio
- Helped JPL demonstrate the LiTDI (lithium 2-trifluoromethyl-4,5-dicyanoimidazole) salt
- Developed pouch cell design for reference electrodes
- Worked with conductive binder from LBNL scaled up by MERF
- Held numerous discussions with materials suppliers regarding their materials
- Initiated electrode thickness study
- Expanded electrochemical model for interfacial impedance and bulk transport
- Determined influence of current rate on LMR-NMC
- Created spreadsheet data analyzer
- Determined influence of PVDF separator

Explore Influence of Silicon Particle Size

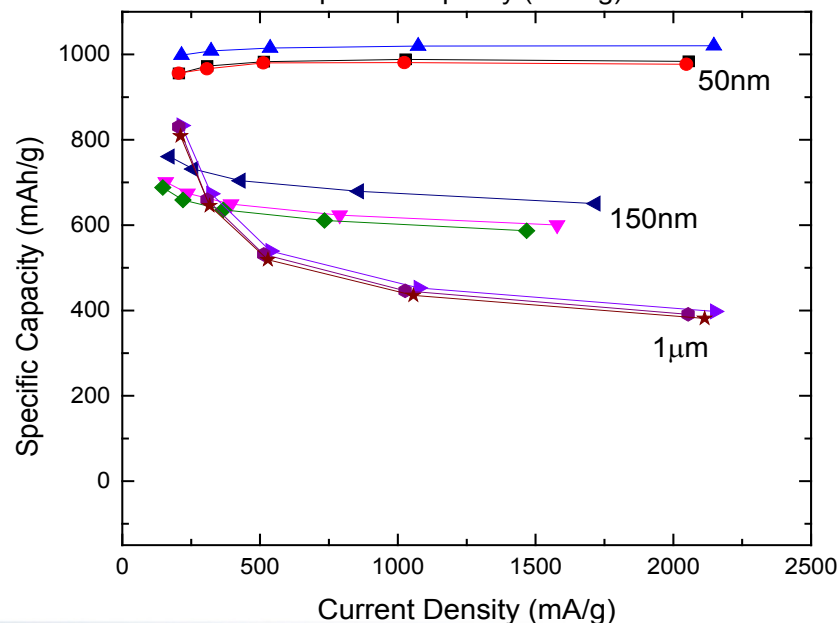
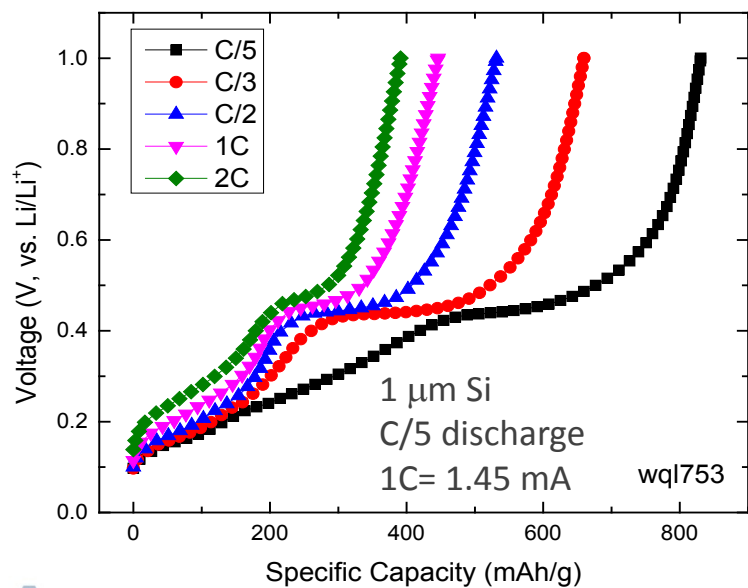
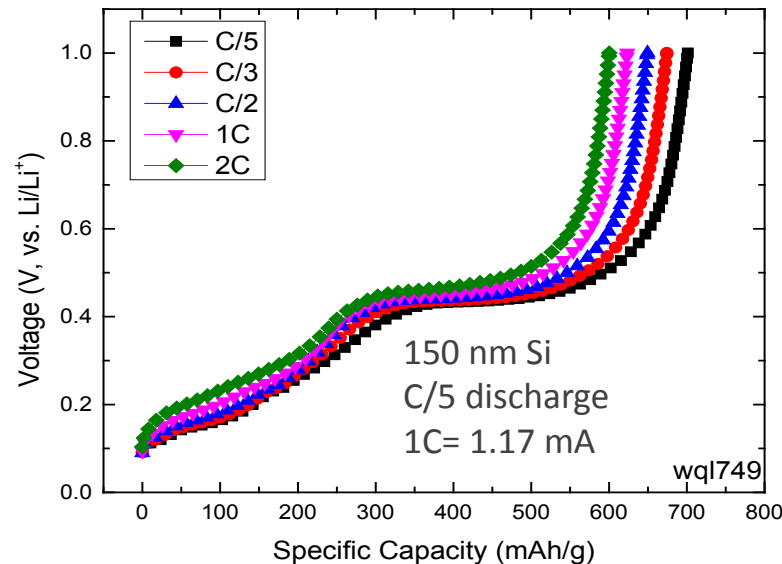
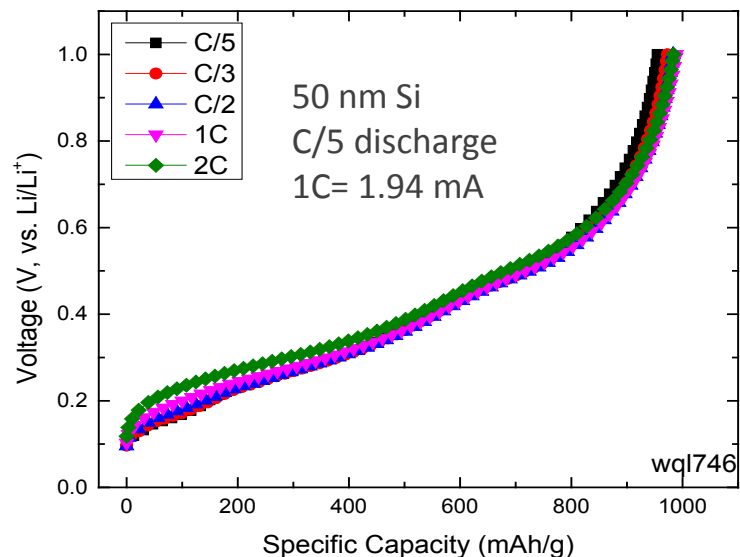
Using Open Source of Silicon from American Elements

Electrode	Composition (Si/Graphene/PAA)	Particle size of Si (μm)	Loading of active material (mg/cm^2)
1	20:60:20	0.05	1.17
2	20:60:20	0.15	0.92
3	20:60:20	1	0.86

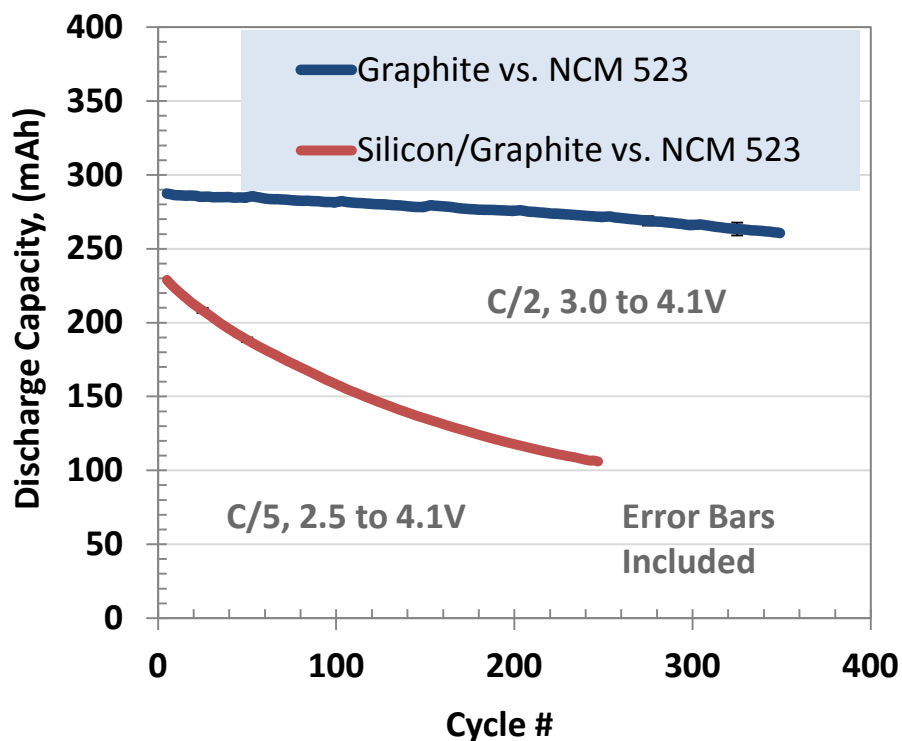
- Silicon from American Elements
- Graphene from XG Sciences
- Solvent: PGME
- Slurry preparation following procedure suggested by XG Sciences
- Electrolyte: 1.2M LiPF_6 EC/EMC (3/7 wt.) with 10% FEC
- Separator: Celgard 2325
- Voltage window: 0.01 V to 1V



Silicon Nanoparticles Give Best Results But are Costly and Can Be More Difficult to Handle



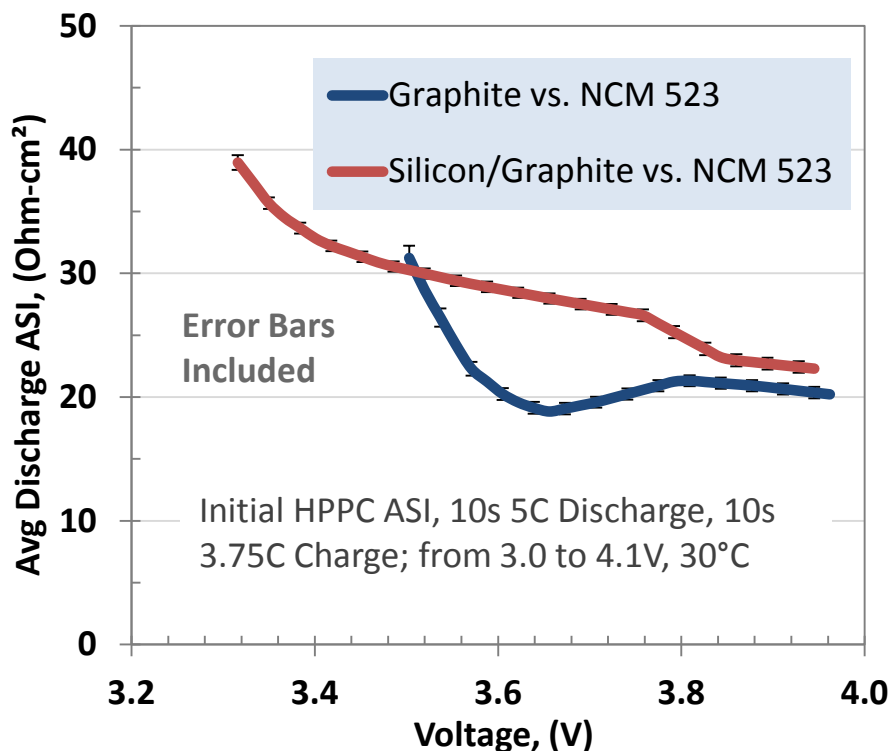
First Pouch Cell Build Using Silicon for Scoping Purposes



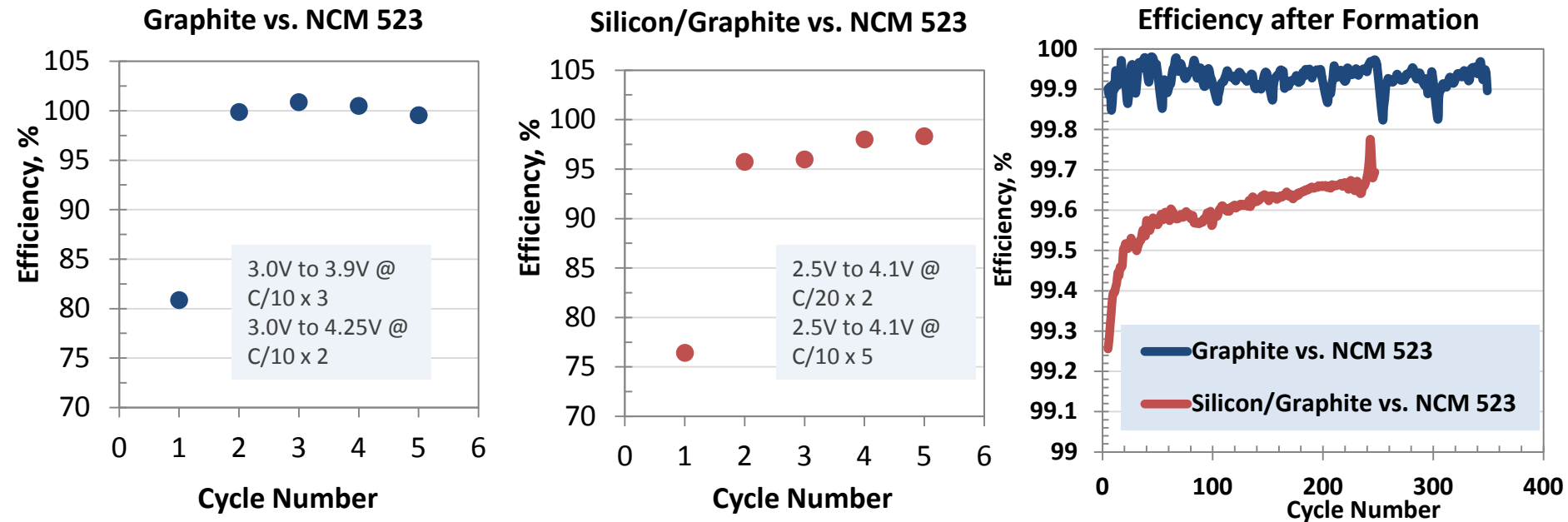
- These silicon cells suffered from large initial capacity loss and rapid capacity fade.
- Some signs of gas generation as cell cycled.

DOE-EERE Vehicle Technologies Program

- Selected 130 nm spherical silicon from Nanostructured & Amorphous Materials (NanoAmor), which is an open source of Si
- Anode: Si/SFG6/C45/LiPAA/Gum (15/73/5/6/1)
- Cathode: Toda NCM523
- Electrolyte: 1.2 M LiPF₆ in EC:EMC (3:7 wt.) + 10 wt.% FEC additive



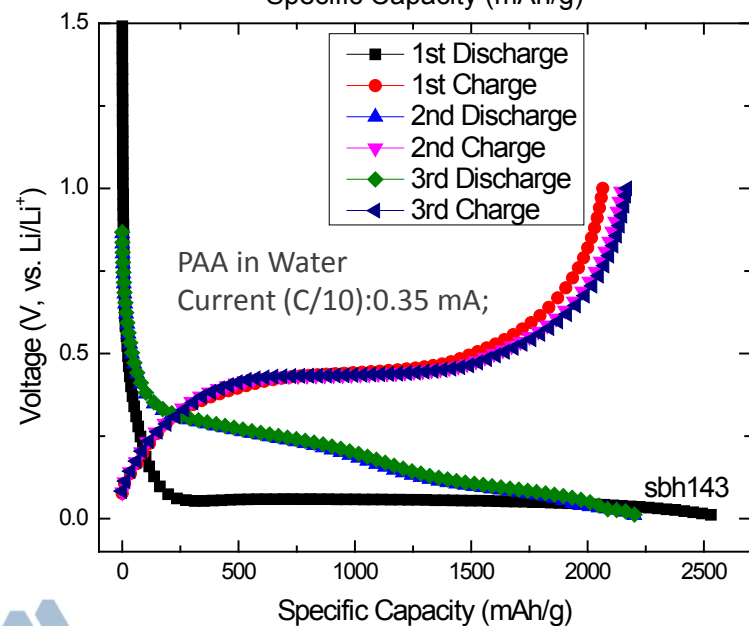
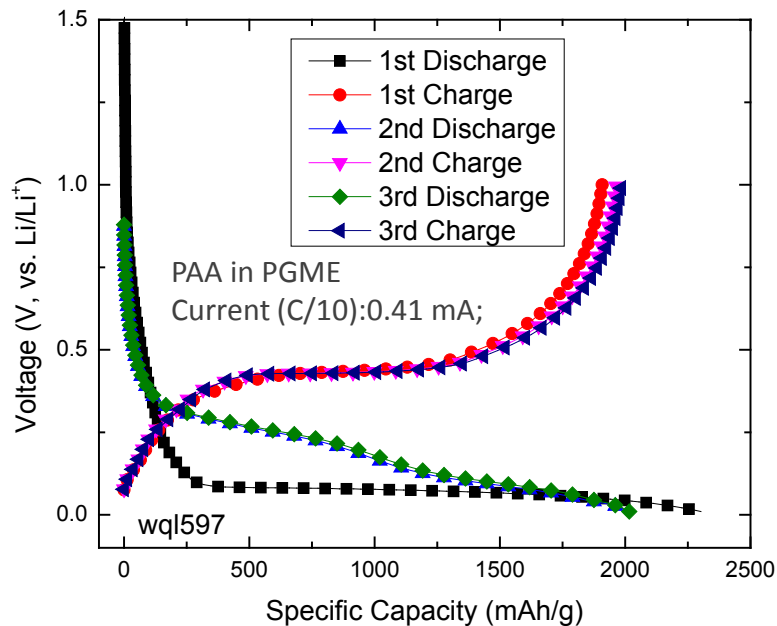
Si Pouch Cells Indicate More Work Needed on SEI Layer



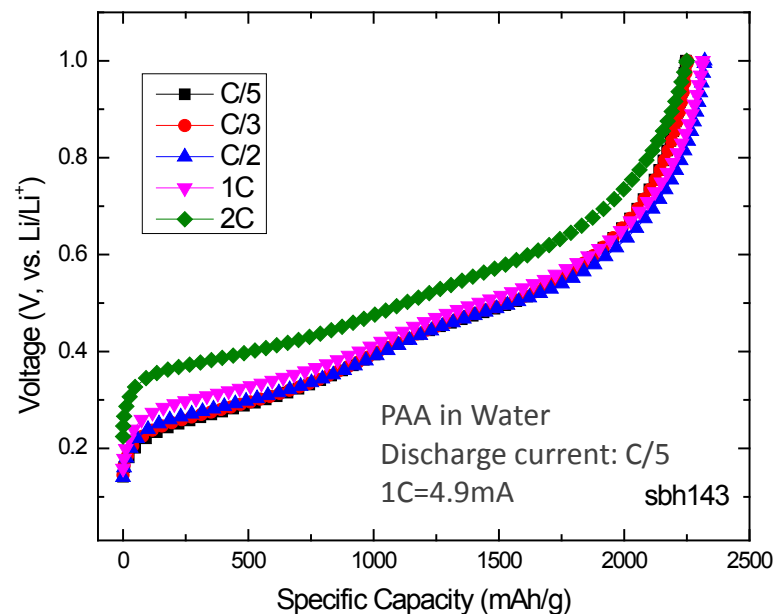
Graphite vs. NCM523 Formation (Average Data)				
Cycle (#)	Charge Cap. (mAh)	Discharge Cap. (mAh)	Coul. Eff. (%)	Cap Loss (mAh)
1	275	222	80.9	53
2	226	226	99.9	0
3	229	231	100.9	-2
4	336	338	100.5	-2
5	345	343	99.6	2
		Sum ->	51	

Silicon/Graphite vs. NCM523 Formation (Average Data)				
Cycle (#)	Charge Cap. (mAh)	Discharge Cap. (mAh)	Coul. Eff. (%)	Cap Loss (mAh)
1	322	246	76.4	76
2	266	255	95.7	11
3	255	245	96.0	10
4	248	243	98.0	5
5	244	240	98.3	4
		Sum ->	106	

Collaboration with XG Sciences on Si-Composite Anode



- Received silicon-composite and graphene powders from XG Sciences
- Performed joint coatings at Argonne
- Converted XG Sciences' PAA binder system based on PGME to water-based PAA system to better meet industry practice.

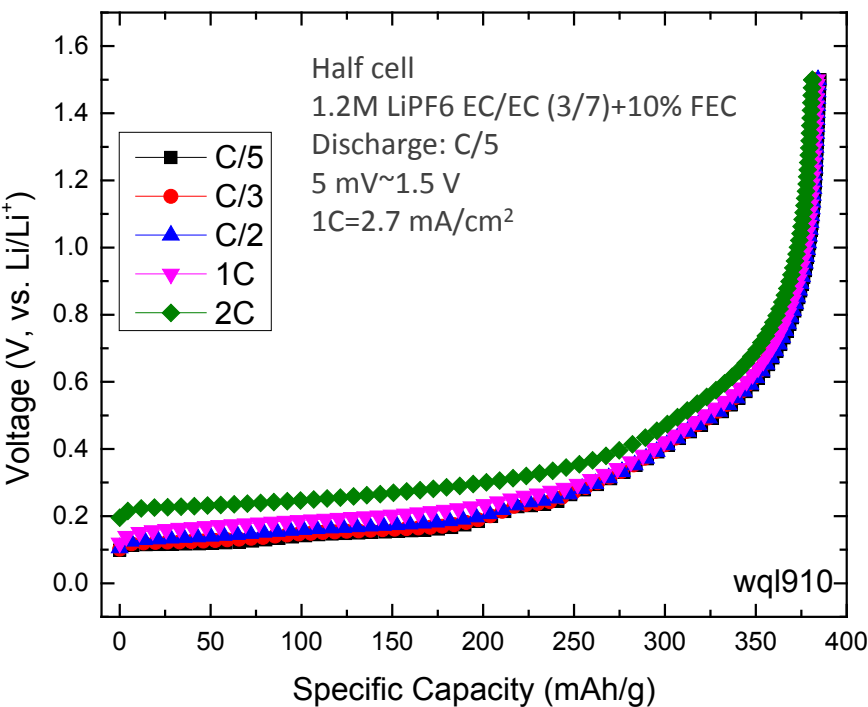
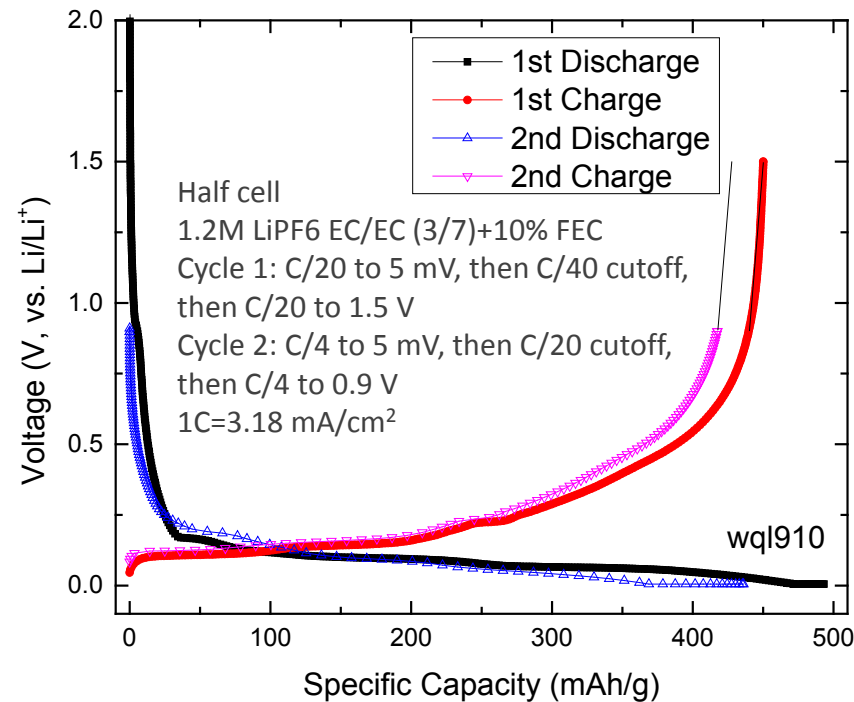


Si-Composite/Graphene/PAA=70:10:20



Collaboration with 3M on Si-based Alloy Anode

- Received powders, double sided electrodes, and process advice from 3M
- Made single stack pouch cells



Information on formation cycles

Electrode	1 st CC (mAh/cm ²)	1 st CC mAh/g ¹	1 st DC (mAh/cm ²)	1 st DC mAh/g ¹	ICL* (%)	2 nd CC (mAh/cm ²)	2 nd CC mAh/g ¹	2 nd DC (mAh/cm ²)	2 nd DC mAh/g ¹	ICL* (%)
Ave.	2.84	461.09	3.1	504.34	8.58	2.7	438.52	2.79	453.85	3.39

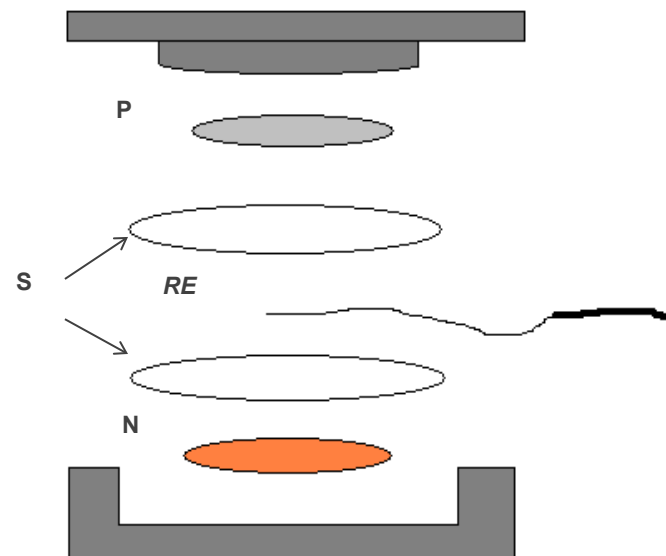
*ICL: Irreversible Capacity Loss

¹ based on materials excluding LiPAA.



Three Major Contributors to Energy Fade of LMR-NMC

- **Voltage fade**
 - Arises from crystal structure changes in the oxide
- **Impedance rise**
 - Mainly at the positive electrode
 - Electronic and ionic contributions
- **Capacity fade**
 - From Li trapping in negative SEI
 - Originates at the positive



ES188, Abraham

Voltage fade contributes ~10% to energy fade.

Impedance rise & capacity fade contribute the rest, which implies more room for improvement with electrode/electrolyte optimization.

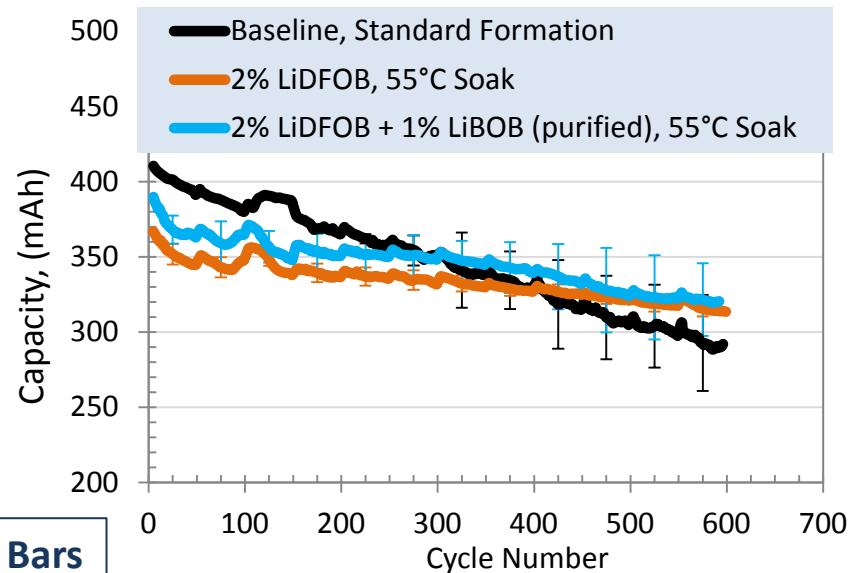
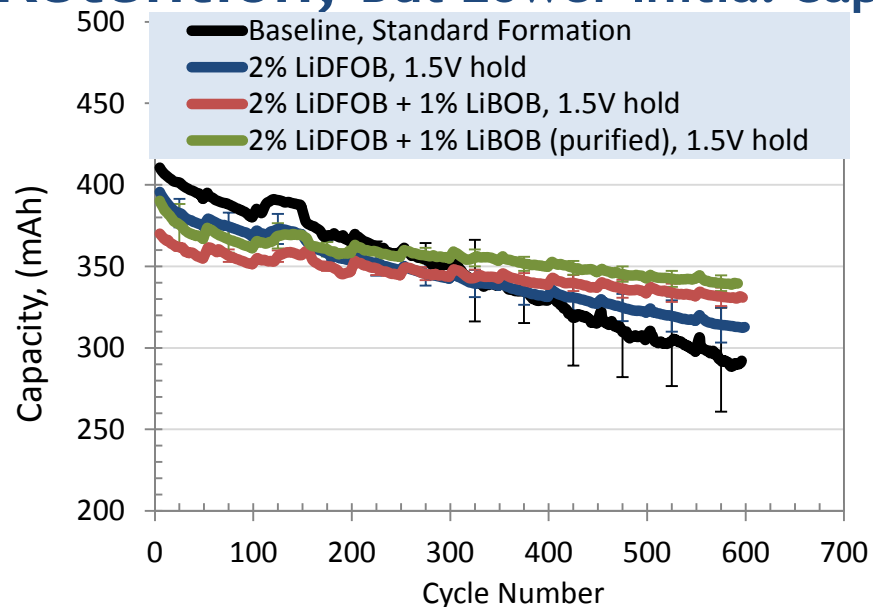
Trask, et al., *J. Power Sources* **259** (2014) 233-244.

Improve Life of LMR-NMC (Toda HE5050) with Additives

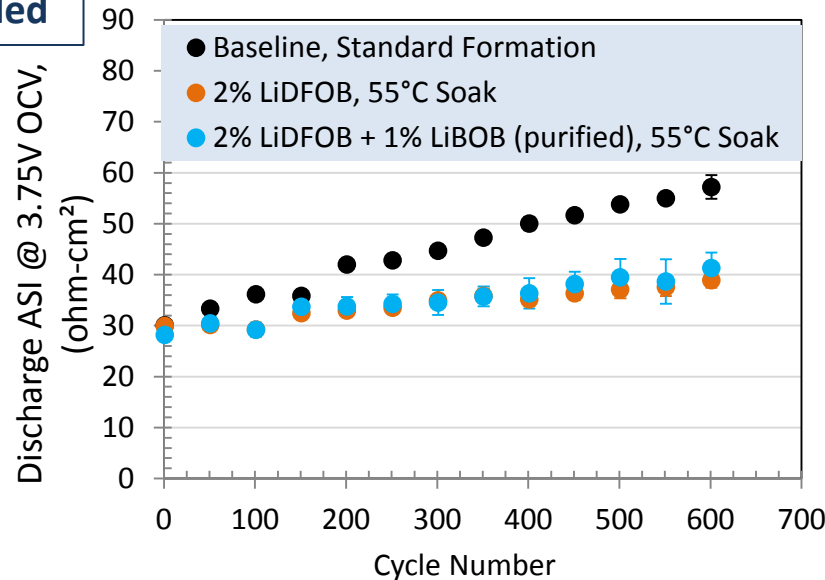
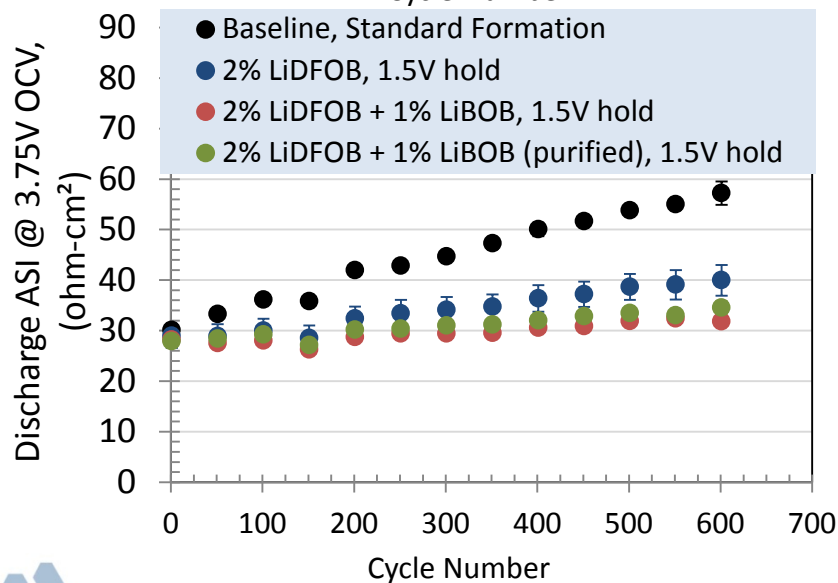
- Earlier work with coin cells showed electrolyte additives benefited performance at 4.7 V
 - Pouch cells at 4.4 V showed less clear benefit
 - Investigate difference
 - Wetting time (24 h for pouch at 30°C)
 - Tap charge showed rxn near 2V
 - Modify formation
 - Limit tap charge to 1.5 V for 15 min; soak for 24 h at 30°C
 - No tap; use 55°C soak
- 1.2M LiPF_6 in EC:EMC (3:7 wt.%) (Baseline)
- LiDFOB made by MERF
 - LiBOB made by Chemetall
 - LiBOB made by Chemetall (purified by MERF)

- Cycle Life Testing:
- C/20 then 47 cycles at C/2
- HPPC with 5C Disch. Pulse, 3.75C Chrg. and repeat
- 2.5 - 4.4V
- 1C-Rate: 375 mAh
- 30°C
- Series are average data
- Error bars are $\pm\sigma$

Electrolyte Additives Stabilize SEI and Improve Capacity Retention, But Lower Initial Capacity



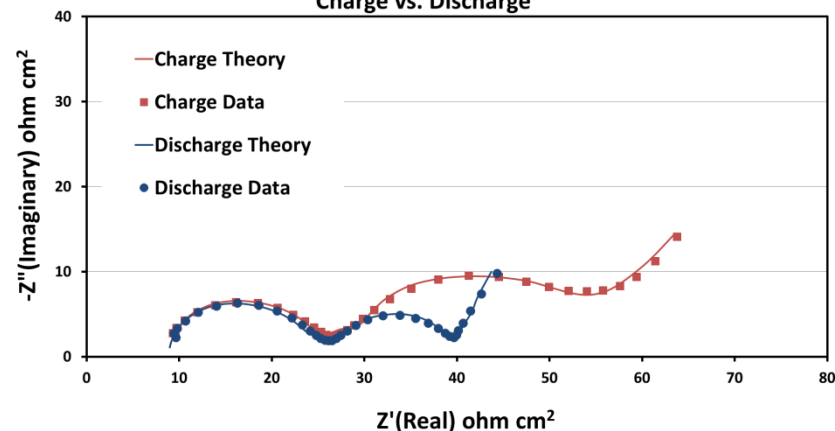
Error Bars Included



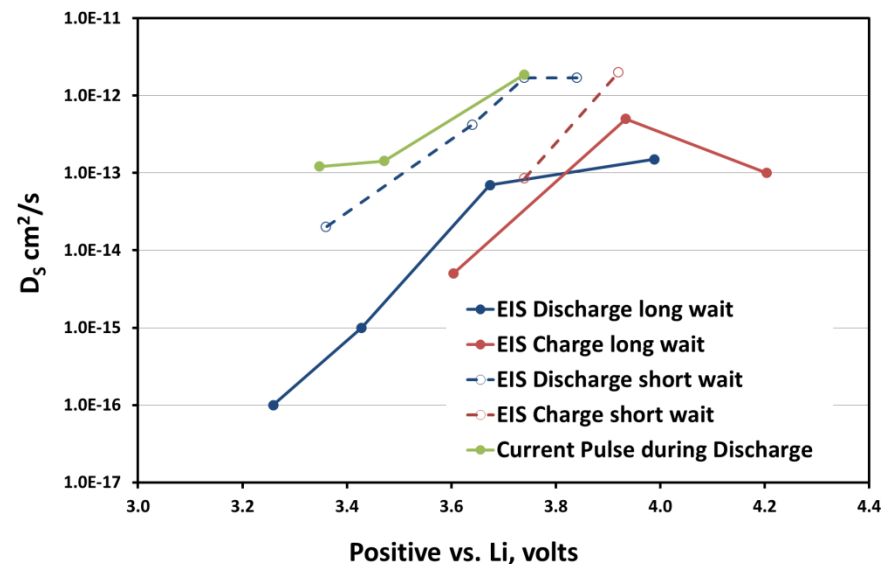
Electrochemical Modeling of LMR-NMC Electrodes

- A system of differential and algebraic equations describing the transport, thermodynamic, and kinetic phenomena are solved to determine current, potential, and concentration distributions within materials, interphases, electrodes, and cells during operation.
- Activities integrated with other CAMP efforts and Voltage Fade studies.
- Focus this year on LMR-NMC electrode hysteresis and impedance effects.
- Electrochemical model used to relate impedance and current pulse studies to changes in transport and reaction parameters with voltage, SOC, time, and charge vs. discharge to gain insight into the fundamental phenomena occurring in LMR-NMC materials.

LMR-NMC Electrode Impedance
(100kHz-10mHz) at 3.74 volts vs. Lithium
Charge vs. Discharge



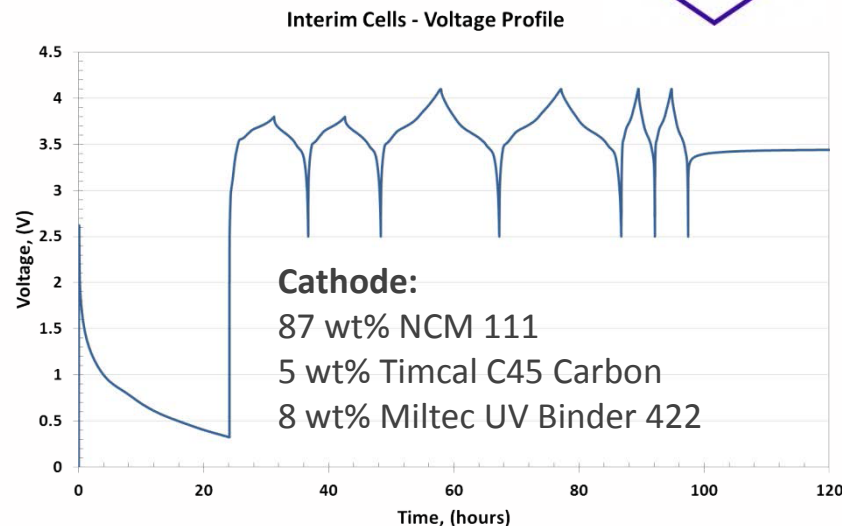
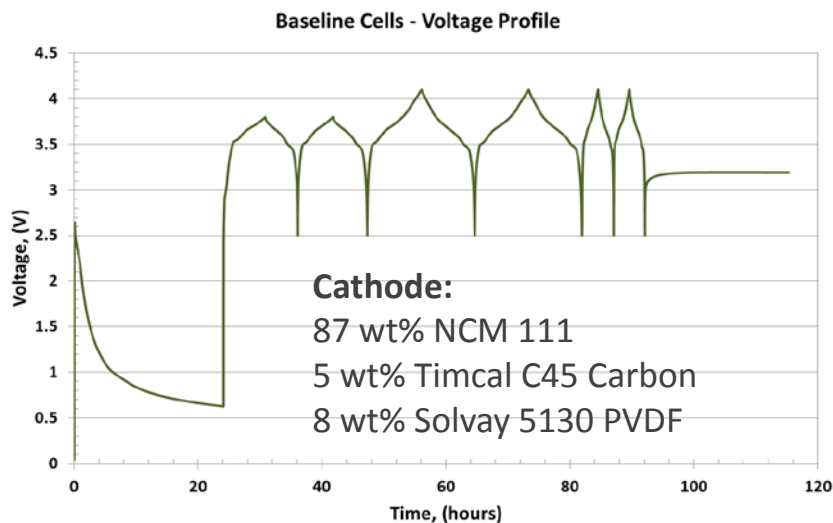
ES189, Dees



CAMP Support of DOE-EERE Award Recipients

Miltec UV (Ultraviolet and Electron Beam Cured Binder Systems to Reduce Cost):

- Baseline PVDF A-12 graphite electrodes and PVDF NCM111 electrodes made
- Baseline and Interim xx3450 pouch cells made and delivered to INL for testing



Argonne (High Energy Electrochemical Couple for EVs):

- Baseline Si composite electrodes and NCM622 electrodes made
- Baseline xx3450 pouch cells made and delivered to INL for testing

Argonne (Electrolyte with High Voltage, Temperature, and Safety for PEVs):

- Graphite electrodes and various cathodes (5V, HE5050, NCM) made
- Baseline xx3450 pouch cells will be made in near future for testing at INL

Penn State (Silicon Alloy-Carbon Composite Anode Coupled with Ni-rich Cathode for PEVs):

- Si-Graphite and NMC electrodes made for initial electrolyte development

Reviewer Comments from 2013 Annual Merit Review

- *Some reviewers commented on “scarcity of statistical data in presentations, and elaborated that it is a standard practice in the battery industry to include the error bars (determined from multiple cell measurements)...”*
- This was also recognized by the CAMP researchers and significant effort was devoted to creating a spreadsheet based data analyzer to more easily mine the data from multiple cells in a build. Error bars with one-sigma are included in many of the plots.
- *Another reviewer “stressed that the standard practice of the industry is to vary the formulation for trial materials to observe the sensitivity of the material to the formulation. In fact, the reviewer observed that after some early trial formulations, it seems that a single formulation has been adopted.”*
- The CAMP Facility is often faced with issue of splitting effort on electrode optimization and effort on new material demonstration. We agree that further refinement of the electrode formulation will improve the material performance, and try to do this in the background for materials of special importance.
- *Another reviewer stated “that the 3M work in this area may be close to providing a commercial solution. The reviewer suggested attempting to work with materials from and to seek advice from 3M, as their materials become available.”*
- This year was more successful in obtaining silicon materials from commercial developers. We now have ample quantities of silicon-based powders, electrodes, and processing advice from 3M and XG Sciences.

CAMP Electrode Library Serves Battery Community

- The Electrode Library serves as a supply of standard electrodes that are designed to be interchangeable with one another (capacity matched).
- Electrodes can be made with as little as 50g of experimental material, and can be made to match an existing counter electrode.

Cathodes Available:

LMR-NMC (HE5050)
 NCA
 5V Spinel ($\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$)
 NCM 523
 NMC 111

Coming Soon:

LCO
 LFP
 4V Spinel (LiMn_2O_4)
 NCM 424
 NCM 622

	Electrodes Delivered			
	Jan-Dec 2013		Jan-Apr 2014	
Argonne	72	18%	45	21%
Other Labs	132	33%	71	33%
Universities	66	16%	28	13%
Industry	134	33%	73	34%
Total	404		217	

Anodes Available:

Superior Graphite 1520P
 Phillips 66 A12 Graphite
 LTO
 Hitachi MAG-10
 MCMB

Coming Soon:

Hard Carbon
 MCMB G-15
 Timcal KS-6-Li
 Si/Graphite Blended
 Hitachi MAG
 Hitachi SMG



CAMP Facility: Electrode & Cell Fabrication Collaborators

Universities













NORTHWESTERN UNIVERSITY

IOWA STATE UNIVERSITY

Industry















National Laboratories















Work in Progress/Future Work

- Work with Post-Test Facility on determining failure mechanisms in silicon-based cells
- Continue electrode and baseline/interim cell builds for DOR-EERE Award recipients
- Conduct electrode and cell builds to improve the performance of silicon-based cells with LMR-NMC cathodes
 - Using silicon materials from 3M, XG Sciences, NanoAmor, American Elements
 - Using LMR-NMC from MERF, Toda, and others
- Continue electrode thickness study with Oak Ridge and industry
- Continue development of electrolyte additives for high energy cells
- Continue development of Gr-Si electrode electrochemical model
- Continue work with MERF on demonstrating scaled-up coated LMR-NMC cathodes (with JPL) and conductive binders for silicon (with LBNL)
- Supply silicon-based pouch and 18650 cells to SNL for thermal abuse testing

Summary

- Several sources of battery grade silicon powders were secured
- A silicon-based pouch cell build was conducted with key concerns identified:
 - Large initial capacity loss and rapid capacity fade observed (Coulombic efficiency concerns)
 - Some gas generation during life noted
 - Volume expansion a concern (must be less than 10% for most applications)
 - More electrode optimization and SEI Formation work needed!
- Secured Superior Graphites' SLC1520P as new CAMP graphite anode baseline
- Pouch cell builds confirmed electrolyte additives improved capacity retention and impedance rise for LMR-NMC cells with modified formation protocols, but at a cost of initial capacity
- Fabricated interim pouch cell build for DOE-EERE Award – Miltec UV
 - Delivered to INL for testing
- Fabricated baseline electrodes and pouch cell for DOE-EERE Award – Argonne (Amine)
 - Delivered to INL for testing
 - Supplied electrodes for other recent DOE-EERE Award recipients
- Supplied numerous electrodes via Electrode Library and expanded its offerings
- Determined effect of Negative to Positive capacity ratio

Contributors and Acknowledgments

Argonne CAMP Team

- | | |
|--------------------|------------------|
| ▪ Andrew Jansen | ▪ Shabbir Ahmed |
| ▪ Dennis Dees | ▪ Qingliu Wu |
| ▪ Bryant Polzin | ▪ Martin Bettge |
| ▪ Steve Trask | ▪ Ye Zhu |
| ▪ Wenquan Lu | ▪ Joseph Kubal |
| ▪ Nancy Dietz-Rago | ▪ Huiming Wu |
| ▪ Daniel Abraham | ▪ Tony Burrell |
| ▪ Kevin Gallagher | ▪ Khalil Amine |
| ▪ Javier Bareno | ▪ Paul Nelson |
| ▪ Ira Bloom | ▪ Gary Henriksen |

Outside Argonne

- Chris Orendorff (SNL)
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- Claus Daniel (ORNL)
- Gao Liu (LBNL)
- Robert Kosteki (LBNL)
- Jai Prakash (Illinois Institute of Technology)
- Ivan Petrov (University of Illinois)
- Alex Wei (Purdue University)
- Yan Li (University of Rochester)

Research Facilities

- Materials Engineering Research Facility (MERF)
- Post-Test Facility (PTF)
- Electrochemical Analysis and Diagnostic Laboratory (EADL)
- Center for Nanoscale Materials (CNM)
- Advanced Photon Source (APS)

Industry

- XG Sciences
- 3M
- Toda America/Kogyo
- Superior Graphite
- Johnson Controls
- JSR Micro
- Zeon Chemicals

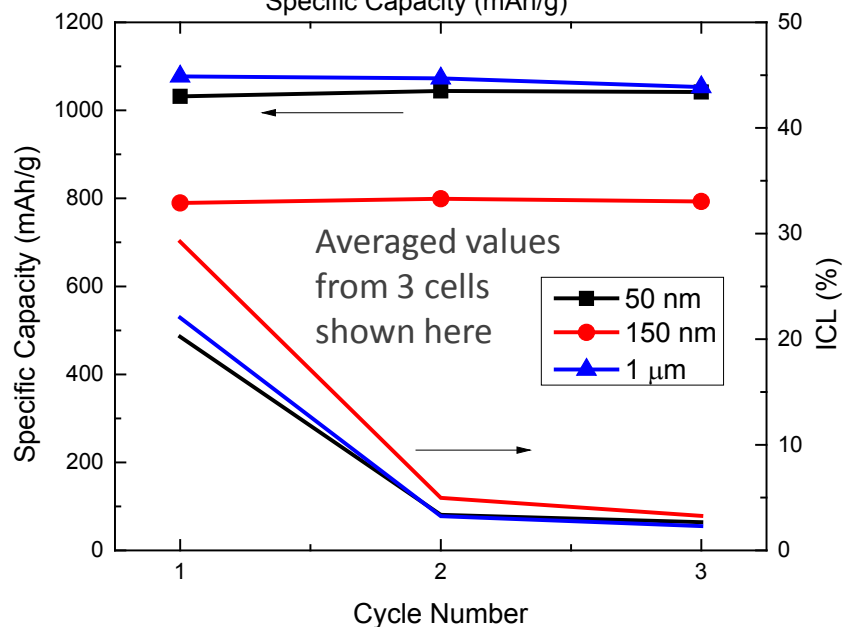
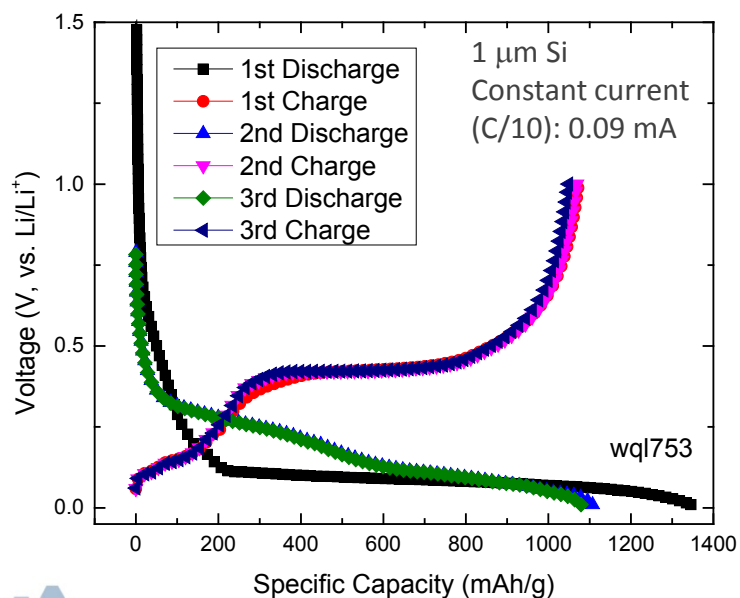
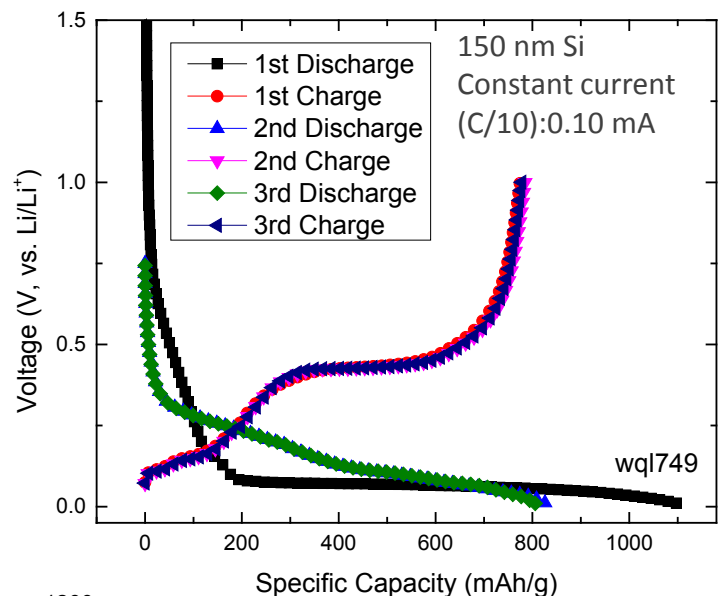
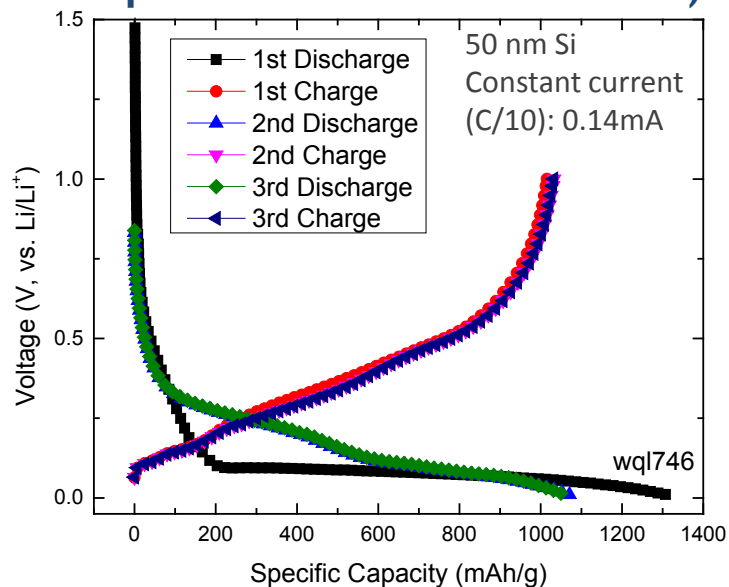
Support from Peter Faguy and David Howell of the U.S. Department of Energy's Office of Vehicle Technologies is gratefully acknowledged.

Technical Back-up Slides

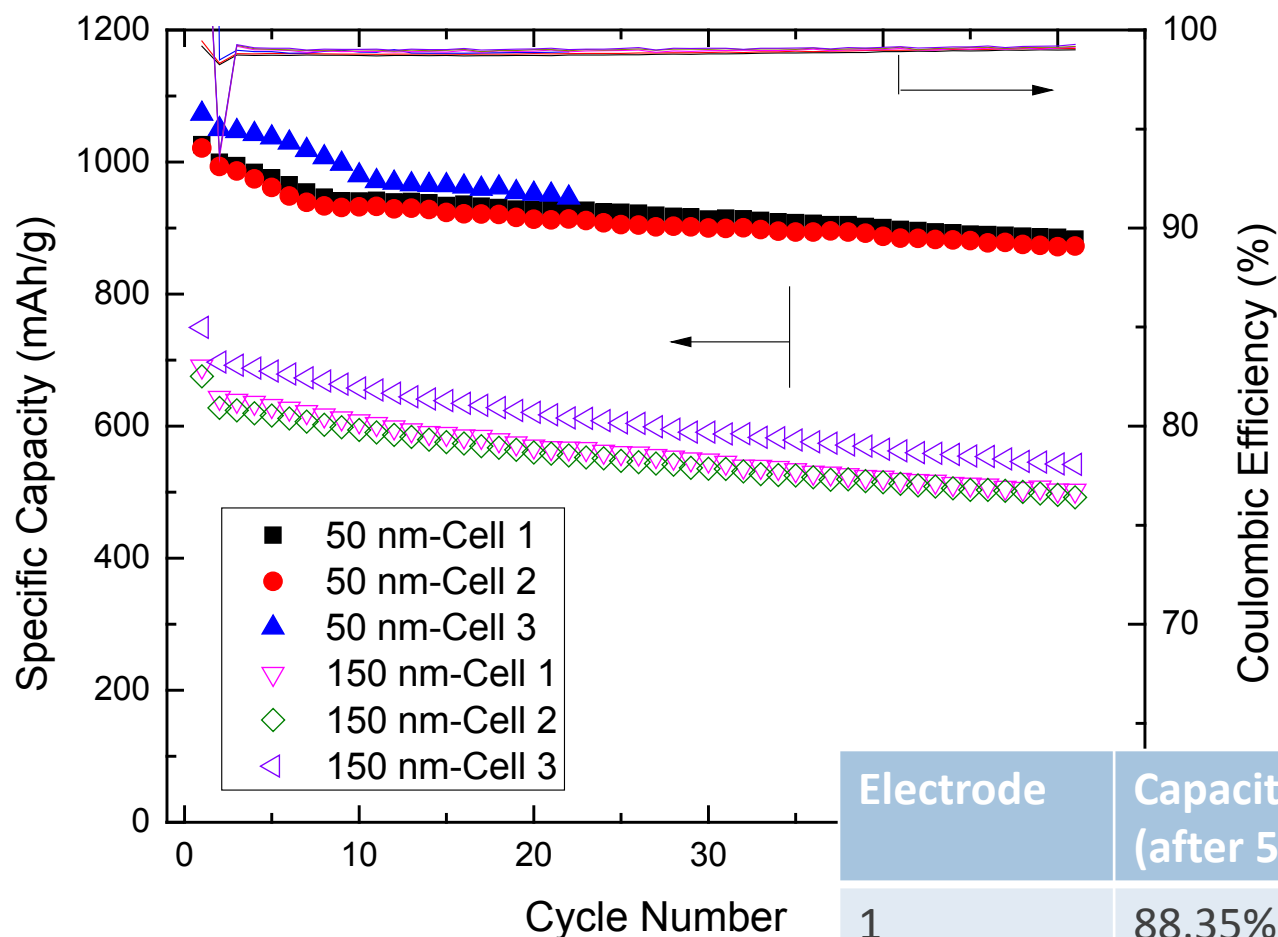
The following slides are available for the presentation and included in the DVD and Web PDF files released to the public.

Formation Cycles for American Elements Silicon vs. Li

(Si/Graphene-XG/PAA=20/60/20)



Cycle Life of American Elements Silicon vs. Li



Composition 1: 20 Si/60 graphene/20 PAA

Electrode

Capacity retention
(after 50 cycles)

1

88.35%

2

78.12%

3

Failed Early



Addition of FEC and Limiting the Extent of Lithiation Enhances Cycle Life

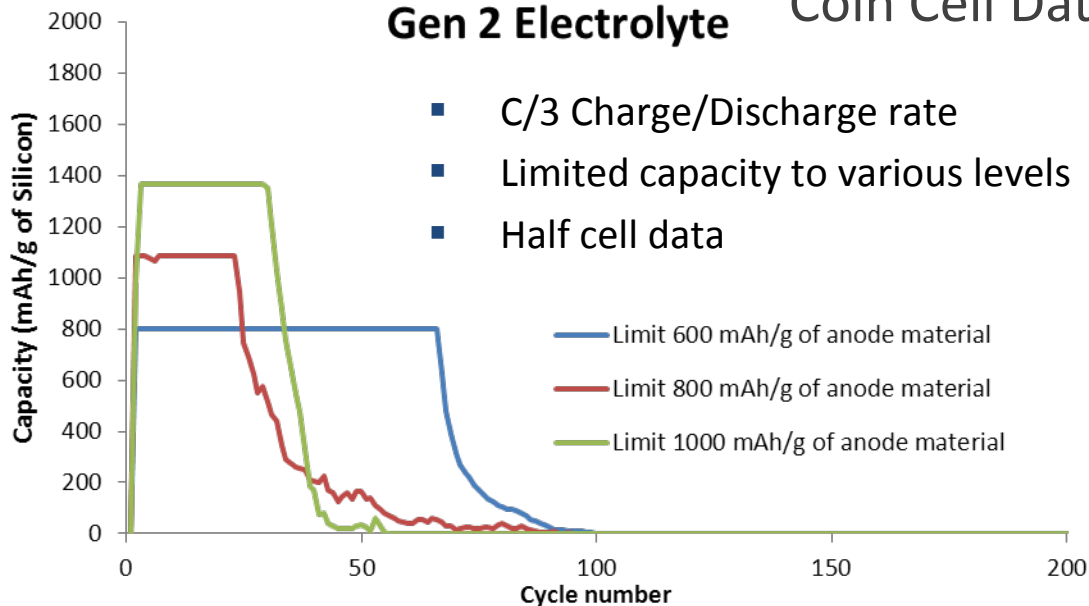
Current work being done

- Si and Si/graphite composites
- Electrolyte additives (FEC)
- Different Binders
- Limiting Capacities/Voltage
- Range of Silicon morphologies
 - 100 nm to 10 μ m range
- Slurry additives
 - (Acids, bases, thickening agents)

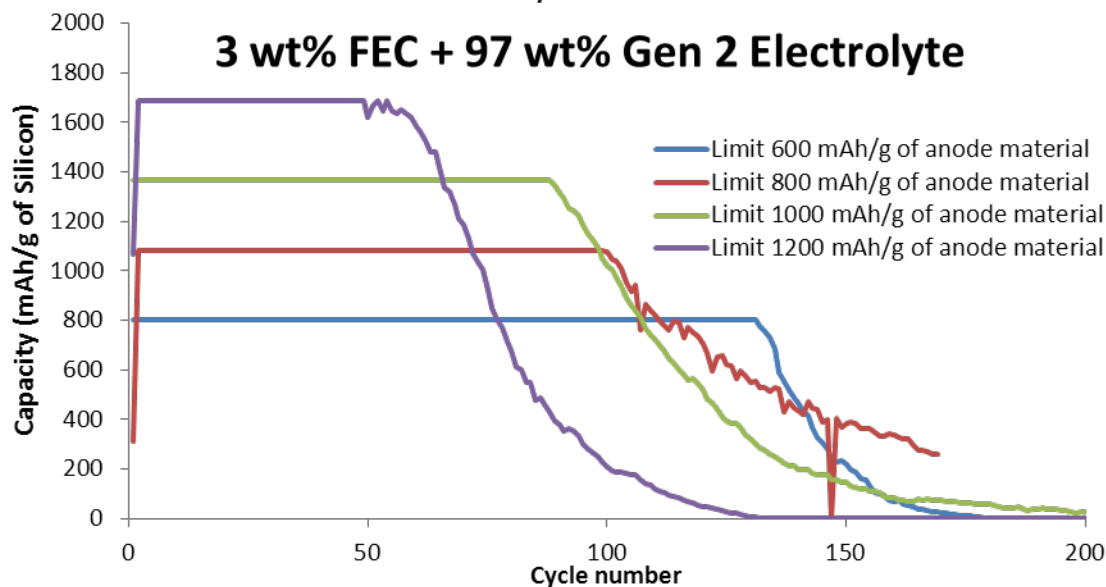
Electrode Composition

- 76% Silicon
- 14% Sodium Alginate
- 10% Super P Carbon
- Citric acid buffer

Gen 2 Electrolyte Coin Cell Data



3 wt% FEC + 97 wt% Gen 2 Electrolyte



Approaches to designing long-life cells

- **Optimize electrode composition and fabrication conditions**
 - High-quality electrodes and cells are fabricated in our Cell Analysis Modeling and Prototyping (CAMP) Facility
- **Alumina-coat the positive electrode or the oxide particles**
 - Oxide materials and coatings are available through our Materials Engineering Research (MERF) Facility
- **Use one or more electrolyte additives, such as LiDFOB, LiBOB, and TTSP**
 - Additives can be synthesized in MERF and their effects examined in our Post-test Facility



CAMP Facility Team Approach

